COMPARISON OF APPROACHES FOR MONITORING H-DONOR CONTENTS
UTILISING REPRESENTATIVE MODEL COMPOUNDS

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ABSTRACT

The content of donatable hydrogen in hydrogenated samples of phenanthrene,
pyrene, fluorene, 1-methylnaphthalene and 2-methylnaphthalene have been calcu-
lated from ^{13}Cnmr spectroscopy, gas chromatography and a chemical test using
sulphur as an hydrogen acceptor. Good agreement between the three approaches
was found for all the samples except hydrogenated fluorene where the value
from the sulphur approach was much higher. However, the ease of carrying out
the sulphur approach would suggest that it is a good method for monitoring the
donatable hydrogen content of process recycle solvents.

INTRODUCTION

As well as producing good conversions to low boiling point material, a coal
liquefaction process on present concepts needs to regenerate its own solvent
which should have a content of hydrogen donor compounds sufficient to maintain
effective dissolution of coal. In two stage liquefaction processes the solvent
is regenerated during the second stage where the coal liquid is catalytically
hydrocracked. Conditions must be set in this second stage to ensure that the
solvent fraction mass balance and its hydrogen content are maintained on recyc-
ling the solvent to the first dissolution stage. Consequently, monitoring the
amount and changes in composition of the recycle solvent is an important role in
liquefaction processes.

Since the recycle solvent fraction contains many different compounds, a detailed
assessment of changes in composition is difficult. However, an evaluation of the
'dissolving power' can be made if the hydrogen donor content of the recycle
solvent is measured. Several methods have been proposed for measuring the
hydrogen donor content with probably the most popular approach adopting quanti-
tative nmr spectroscopy[1-8]. Amongst the other approaches, the use of hydrogen
acceptors in chemical tests have been suggested. For instance, Bockrath et al[9]
used dibenzylmercury as a source of benzyl radicals to which hydroaromatic com-
pounds would donate hydrogen. Aiura et al[10] used sulphur as the hydrogen
acceptor and found good agreement with results calculated from nmr spectroscopy.

In this paper, a modified chemical test using sulphur is compared with quanti-
tative nmr for hydroaromatic mixtures produced by catalytic hydrogenation of the
parent aromatic compound; the donor content was also estimated from the glc anal-
ysis of the hydrogenated product. The aromatic compounds used were phenanthrene,
pyrene, 1-methylnaphthalene, 2-methylnaphthalene and fluorene whose hydroaromatic
derivatives have boiling points consistent with that of the recycle solvent.

EXPERIMENTAL

Hydrogenation of model aromatic compounds

All the hydrogenations were carried out in a 500ml capacity spinning/falling
basket autoclave manufactured by Baskerville Scientific Ltd and used a 15% Mo/

3% Co commercial catalyst supplied by Akzo Chemie, the Netherlands. Typically, 75g of the model compound were hydrogenated with 5.0g of catalyst at a feed pressure of hydrogen of 10MPa for 2h at 400°C.

Glc analysis of hydrogenated products

The products were analysed as ~1% solutions in cyclohexane using a Perkin Elmer Sigma 3B Dual FID Chromatograph attached to a JJ Model CR 600 Pen Recorder and a LDC Model 300 Peak Area Integrater. 0.5 µl of the solution was injected through a pneumatic seal onto an OV 101, 25 m x 0.32 mm capillary column over a temperature program of 80°C initial temperature and 5°C min^{-1} ramp rate. Identification of the peaks was assisted by gc/ms analysis, kindly carried out by British Coal, Coal Research Establishment.

Nmr spectroscopy analysis

Proton and ^{13}Cnmr spectra were recorded on a Jeol Model PFT-90Q spectrometer fitted with a 10 mm probe. All solutions were made up in chloroform-d and TMS was added as an internal standard for the proton spectra; the chloroform-d peak at 76.99 p.p.m. was used as the standard for ^{13}C spectra. To facilitate quantification of ^{13}Cnmr, the paramagnetic relaxation agent, chromium acetylacetonate was added and 10,000 acquisitions were gathered at a 3s delay between the 90° pulses. A gated decoupling sequence was used during acquisitions.

Chemical testing of hydrogenated products with sulphur

0.2-0.3g (weighed to four decimal places on an analytical balance) was reacted with 0.5g of elemental sulphur in a 10ml capacity bomb-type autoclave (manufactured by Baskerville Scientific Ltd) fitted with a 0-10 bar Schaevitz pressure transducer linked to a digital readout. The bomb was maintained at temperature (250°C) until no further increase in the H_2S pressure was observed. The measured pressure was related to the H-donor content using a calibration graph produced from similar experiments with known amounts of 9, 10 dihydrophenanthrene.

RESULTS AND DISCUSSION

Table 1 shows the contents of starting material, hydroaromatic, saturate and non-donor compounds for the hydrogenated products. Where the glc peaks could not be identified they were assigned to the non-donor heading. For phenanthrene the hydroaromatic content was 50% octa, 31% tetra and 3% dihydrophenanthrene with the remaining 16% being made up of butyltetralin, tetralin and the isomerisation compound cyclohexylmethylindan; of the non-donor compounds 14% was identified as biphenyl. The breakdown of the hydropyrenes was di, 25.5%; hexa, 57.9%; tetra, 5.4% and deca, 11.2%. The hydroaromatic content of the hydrogenated methylnaphthalenes contained both methyltetralins and tetralin and the non-donor compounds mainly consisted of decalin and naphthalene. For fluorene only 80% of the peaks were identified; the hydroaromatic content was all hexahydrofluorene and 49% of the non-donor material was diphenylmethane.

An estimation of the hydrogen donor content was made from glc using the integrated peak areas of the assigned peaks and multiplying by the number of donatable hydrogen. An example of the peak assignment is shown in figure 1 for hydrogenated pyrene. The values calculated are shown in table 2 as wt% donatable hydrogen product. The estimation of donatable hydrogen from ^{13}Cnmr spectroscopy followed

the method of Clarke et al[1] and the calculated results are shown in table 2 which also contains the values determined from the sulphur chemical test and values of aromaticities calculated directly from ^{13}Cnmr spectroscopy; aromaticities were also calculated indirectly from proton nmr spectroscopy (following Brown and Ladner[11]) and from glc analysis (denoted by the heading theoretical). A sample ^{13}Cnmr spectrum for hydrogenated 1-methylnaphthalene is shown in figure 2 which clearly shows the aromatic and aliphatic regions separated by the peaks from the chloroform-d solvent.

Agreement between the three approaches is generally good, the S-method tending to produce the higher values and ^{13}Cnmr the lower values. The donatable hydrogen content obtained from glc is compared with that from nmr in figure 3 and with that from the S-method in figure 4. It can be seen that for figure 3 the points tend to the left of the theoretical line and for figure 4 they tend to the right of the line.

The values for hydrogenated fluorene do show a wide variation compared with the other samples. The value obtained from glc could be an underestimate because of the relatively large proportion of the peaks that remained unidentified. Some of these peaks could have resulted from hydroaromatic compounds and might account for the difference between the glc and nmr spectroscopy methods but is not large enough to account for the difference to the value for the S-method. However, the product from the sulphur test did contain some black insoluble material, probably indicative of the occurrence of some polymerisation. Glc analysis of the soluble part of the product did show the formation of some higher boiling point material (retention time 1918s) and the disappearance of some of the lower boiling point material. Therefore, other reactions than dehydrogenation of hexahydrofluorene occurred; these reactions may have produced gaseous alkanes which would contribute to the pressure rise. Unfortunately, analysis of the gas mixture after the reaction was not possible. Further experiments are now in hand to assess the other reactions occurring but the fact that these reactions occur even at 250°C (cf 400°C used for coal dissolution) may suggest that hydrofluorenes may not be good hydrogen donors.

CONCLUSIONS

Apart from the hydrogenated fluorene, the chemical test method using sulphur as an hydrogen acceptor has proved to be a good method for determining donatable hydrogen contents. The method requires only a small amount of sample, can be carried out in a few hours and used relatively inexpensive material. The glc approach would be unsuitable for recycle solvents because of the complex chromatograms and the difficulty in identifying all the peaks. The ^{13}Cnmr approach needs more expensive equipment, a separate saturates determination and will take much longer in order to accumulate a good spectrum. The S-method has been tried with recycle solvents and has, on first estimations, shown good agreement with values calculated from ^{13}Cnmr[12]. The method is also more representative of the situation in coal dissolution in that it places the recycle solvent under hydrogen donation conditions.

ACKNOWLEDGEMENTS

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12. Bate K and Harrison G, to be presented at Int. Conf. Coal Science, Tokyo, Japan, Oct 1989.

STARTING COMPOUND	G.L.C. Analysis of Hydrogenated Product (wt%)			
	Compound remaining	Hydro-Aromatic	Saturates	Non-donor
[structure: pyrene]	24.2	72.2	-	3.6
[structure: chrysene/triphenylene]	28.3	58.1	3.0	10.6
[structure: methylnaphthalene, CH₃]	16.7	74.7	4.8	3.8
[structure: methylnaphthalene, CH₃]	26.4	59.2	4.5	9.9
[structure: fluorene]	28.6	25.8	-	45.6

TABLE 1. ANALYSIS OF THE HYDROGENATED MODEL COMPOUNDS

STARTING COMPOUND	DONATABLE HYDROGEN (%)			AROMATICITIES		
	* S METHOD	G.L.C.	^{13}C N.M.R.	^{13}C N.M.R.	^{1}H N.M.R	THEOR-ETICAL
[structure: pyrene]	1.87	1.84	1.77	0.77	0.85	0.75
[structure: chrysene/triphenylene]	2.09	1.94	1.86	0.75	0.78	0.68
[structure: methylnaphthalene, CH₃]	2.09	2.07	2.08	0.60	0.68	0.63
[structure: methylnaphthalene, CH₃]	1.87	1.65	1.62	0.64	0.69	0.65
[structure: fluorene]	2.44	0.96	1.23	0.61	0.78	0.78

* CHEMICAL DEHYDROGENATION USING SULPHUR AS AN HYDROGEN ACCEPTOR

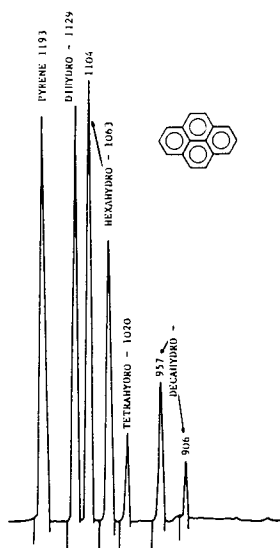TABLE 2 Donatable Hydrogen Content and Aromaticities of Hydrogenated Model Compounds

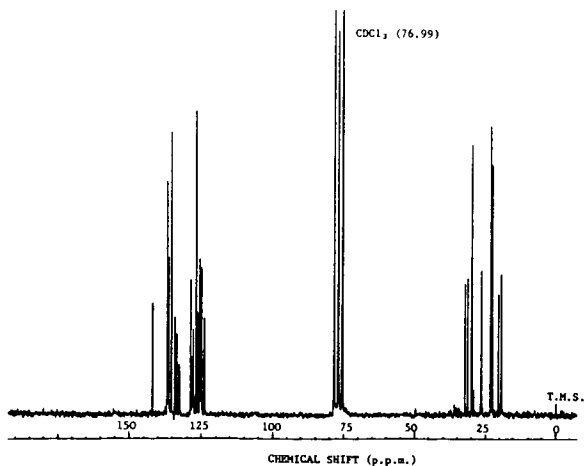FIGURE 1 Gas Liquid Chromatogram of Hydrogenated Pyrene Showing Retention Times in Seconds

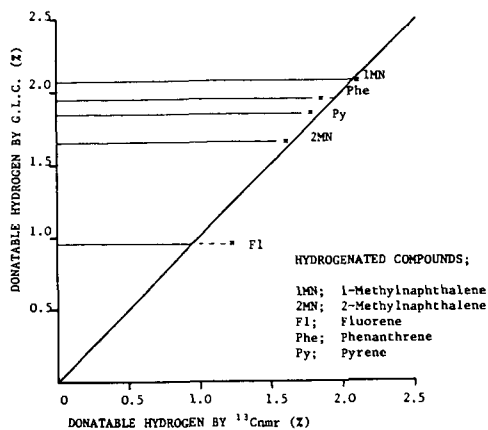FIGURE 2 ^{13}C nmr Spectra of Hydrogenated 1-Methylnaphthalene

FIGURE 3 Comparison of G.L.C. and ^{13}Cnmr for the
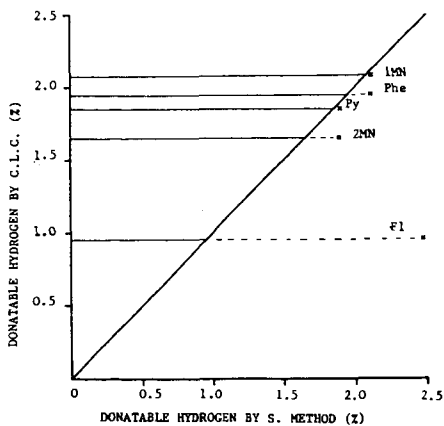Determination of Donatable Hydrogen

FIGURE 4 Comparison of G.L.C. and S Method for
the Determination of Donatable Hydrogen

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